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TITLE OF THE INVENTION

INHOMOGENEOUS SILICAS AS CARRIER MATERIAL

BACKGROUND OF THE INVENTION

Field Of The Invention

The present invention relates to silicas having an inhomogeneous structure or composition, to processes for preparing them, and to their use as carrier material.

Description Of The Background

Readily dispersible silicas are prepared, for example, by the procedure described, for instance, in EP 0 901 986 or EP 0 647 591 by precipitating waterglass with sulfuric acid, followed by drying. The dried products are subsequently ground and/or granulated.

By means of mechanical granulation, any silica can be prepared in dust-free form; however, this additional process step generally brings about a deterioration in the dispersibility of the silica.

In another process, silicas are prepared, likewise by acid precipitation, but are dried by spraying with hot air and at the same time are shaped into beads, which are easily destroyed. Thus EP 018 866 describes the preparation of spray-dried silica having an average particle diameter of more than 80 μm, the particles being solid and possessing a homogeneous structure.

Spray-dried silicas as described in EP 0 018 866 are particularly suitable as carrier

materials, because they are dust-free and possess a high absorbency. The ability to operate without dust being generated is an important criterion for the processing of the silica, because simple processing of the silicas without the need for suction exhaust units is of great economic importance. Besides freedom from dust, the specific surface areas (BET, CTAB) and the oil absorption capacity (DBP) are important for carrier material utility.

In contrast to mechanical granulation, spray drying cannot be used to prepare all silicas in dust-free form.

One type of silica generally does not meet all of the required criteria. Mixtures of two or more types of silica can frequently be prepared, but such mixtures normally generate excessive amounts of dust. A need therefore continues to exist for a silica which at one and the same time covers broad ranges of physicochemical data such as BET or CTAB surface area, and which has good absorbency and generates only low quantities of dust. As already stated, this cannot be achieved for all silicas by means of spray drying or granulation.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a silica that has an inhomogeneous composition and is readily adjustable to meet the requirements that are called for as a carrier and yet has good absorbency and a low fines content.

Briefly, this object and other objects of the present invention as hereinafter will become more readily apparent can be attained by a silica comprising at least two silica fractions, wherein said at least two silica fractions differ by at least 10% in at least one value for BET surface area, CTAB surface area and DBP absorption, the ranges of these three physicochemical properties being as follows:

BET surface area	100 - 900 m^2/g,
CTAB surface area	100 - 500 m^2/g,
DBP absorption	150 - 350 g/100 g.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The silicas of the invention are particularly suitable for use as carrier materials for active substances such as vitamins and choline chloride, for example.

The composition of the silicas, comprising at least two silica fractions, results in a structural inhomogeneity of the silica, which is reflected at the same time in good absorbency and a low fines content and provides the physicochemical data required of the present invention.

Silicas of the invention possess a fines content of not more than 10% with a particle diameter of less than or equal to 63 μm (Alpine sieve residue).

A similar concept is described in EP 0 942 029. There, compositions are described which comprise a precipitated silica in two different aggregate sizes. The different aggregate sizes are employed for the ready dispersibility of the silica in a rubber blend. The different silica fractions of the present invention are not described in these publications; moreover, in the present case a different aggregate size of the silica fractions is of secondary importance. What is of importance in the invention is the differences in the physicochemical data of the two silicas. The use of silicas as carrier materials is not described in EP 0 942 029.

For the purpose of the present invention, a silica fraction refers to different grades of silicas which, owing to different preparation processes or process variants, have a difference of 10% in at least one of the abovementioned physicochemical characteristics. Such a

difference exists preferably for two, particularly preferable three, of these parameters.

The differences in the abovementioned parameters may be obtained by means of different processes of preparing the silica fractions. Accordingly, all, one or more of the silica fractions may be precipitated silicas and/or pyrogenic silicas. In the case of precipitated silicas in particular it is possible to obtain different silica fractions by means of different precipitation processes. Silicas of the invention may also be prepared from fractions of precipitated and pyrogenic silicas.

For precipitated silicas as carrier material, a variety of precipitation methods is known and are disclosed, for example, in EP 0 937 755 and EP 0 643 015. In the examples of the two documents, illustratively, two precipitated silicas from different preparation processes are processed to give inhomogeneous silicas. Such methods can be used in the present invention. It is also possible to combine hydrophobicized silica fractions with untreated silica fractions to give the silica of the invention.

The silica fractions may be precipitated silicas or pyrogenic silicas, and the fractions may be mixed at different steps in the process that are normally conducted in the preparation of silicas.

When using fractions of precipitated silicas, mixing may take place following the precipitation of silicate with an acid, which is normally waterglass, i.e., sodium silicate, with sulfuric acid, by mixing together the precipitation suspensions or the filtercakes obtained following filtration of the suspensions, and also liquefied (resuspended) filtercakes. It is also possible to add ready-prepared, dried or hydrophobicized silica fractions, as solids, to the suspensions or to the filtercakes.

The mixtures obtained in this manner may need to be filtered and dried by a usual

technique. Examples of drying processes are spray drying, nozzle spray drier, rack drier, rotary tube drier, and spin flash drier processes.

Drying may be followed by a final grinding and/or granulation step.

It is also possible to mix the silica fractions in the dry state. This operation may be followed by resuspension, with the above drying steps, and/or by grinding/granulation.

Silicas of the invention may have the following physicochemical data:

BET surface area	100 - 900 m^2/g, preferably 150 - 600 m^2/g
CTAB surface area	100 - 500 m^2/g, preferably 150 - 400 m^2/g
DBP absorption	150 - 350 g/100 g

These physicochemical data relate to the silica of the invention per se, and not to the silica fractions.

In the manner described, the physicochemical data of the silica fractions must differ by at least 10%, preferably by at least 15%, and particularly preferred by at least 20%.

The physicochemical data are determined by the following methods:

BET surface area	Areameter, from Ströhlein, to ISO 5794/Annex D
CTAB surface area	at pH 9 by the method of Jay, Janzen and Kraus in Rubber Chemistry and Technology 44 (1971) 1287
DBP number	ASTM D 2414-88

The invention in addition provides a process for preparing silicas comprising at least two silica fractions, in which at least two silica fractions differ by at least 10% in at one least

one value for BET surface area, CTAB surface area and DBP absorption. The fractions are mixed with one another.

The proportion of the respective fractions in the suspension or of the silica should in each case range from 5 to 95% by weight, based on the dry silica.

The silica is preferably prepared, by spray drying, for example, in a particle form having an average diameter of more than 80 μm, in particular more than 100 μm, particularly preferably more than 200 μm. The suspension may be spray-dried as described, for example, in U. S. Patent 4,097,771.

The silicas of the invention may therefore be used as carrier material, especially for adsorbing liquid active substances.

The silicas of the invention can be used in particular as carriers for vitamins (A, B, C, E), where appropriate in acetate form, proteins, enzymes, choline chloride and the like.

Furthermore, the silica may be used as a support for catalytically active substances.

Moreover, the silicas of the invention may be used in all areas of application in which silicas are customarily used, such as in battery separators, antiblocking agents, flatting agents and paints, paper coating slips or defoamers, for example.

The silica of the invention or the silica fractions may be modified in a known manner, i.e., hydrophobicized, with silanes, with silicone oil and/or with organosilanes.

<u>Procedure for determining the Alpine sieve residue:</u>

To determine the sieve residue, the silica or silicate sample is passed through a 500 μm sieve in order to destroy any devolatilization agglomerates that may be present. Then 10 g of the sieved sample are placed on the air jet sieve, with a 63 μm sieve mesh, and are

sieved at 200 mm water column under pressure. Particles of silica or silicate which settle on the sieve cover of the apparatus are removed by careful tapping on the button of the sieve cover. The sieving operation generally lasts 5 minutes. It is at an end when the residue remains constant, generally evident from the free-flowing appearance. Sieving is then continued for one more minute in order to be on the safe side.

If any agglomerates form, the sieving operation is briefly interrupted and the agglomerates are broken down under gentle pressure using a brush. After sieving, the sieve residue is carefully removed from the air jet sieve and reweighed. The sieve residue is expressed in percent, always in conjunction with the mesh size of the sieve.

Calculation:

$$\% \text{ of sieve residue} = \frac{A \cdot 100}{E}$$

A = final weight in g

E = initial weight in g

Apparatus

Alpine air jet sieve, laboratory type S 200

Vacuum cleaner or fan

Air jet sieve with sieve mesh 63 μm to DIN 4188

Precision balance

Having generally described this invention, a further understanding can be obtained by

reference to certain specific examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

Two silica fractions were prepared, A in accordance with the procedure described in U. S. Patent 1,043,282 or DE 24 47 013 and B in accordance the procedure described in DE 31 44 299, and the suspensions obtained from the precipitations were reacted further in the manner described below.

EXAMPLES

Example 1

The precipitation suspensions of the silica fractions A and B were mixed in a 50:50 ratio. This was done by mixing 80 kg of the precipitated silica A (solids content approximately 46 g/l) with 80 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a nozzle spray drier. The analytical data obtained are compiled in Table 1.

Example 2

The precipitation suspensions of the silica fractions A and B were mixed in a 70:30 ratio. This was done by mixing 112 kg of the precipitated silica A (solids content approximately 46 g/l) with 48 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a nozzle spray drier. The analytical data obtained are compiled in Table 1.

Example 3

The precipitation suspensions of the silica fractions A and B were mixed in a 30:70 ratio. This was done by mixing 43.8 kg of the precipitated silica A (solids content approximately 46 g/l) with 102.2 kg of the precipitated silica B (solids content approximately 64 g/l) in a stirred vessel. The resulting mixture was filtered and the filtercake was liquefied with a small amount of acid and sprayed in a nozzle spray drier. The analytical data obtained are compiled in Table 1.

Example 4

A mixture of the dried silica fractions (50:50) was prepared.

Table 1:

Comparison of the analytical data from Examples 1-4 and of silica fractions A and B:

		Silica fraction A	Silica fraction B	Differences of fractions A:B in %	Example 1	Example 2	Example 3	Example 4
Loss on ignition, DIN	%	5.0	5.0		3.7	2.7	3.4	10.1
Water content	%	5.0	4.5	10	5.3	5.3	5.5	5.6
pH reading		6.5	6.0	7.6	6.2	6.4	6.4	6.6
Conductivity	μS	800	700	12.5	600	740	610	750
BET surface area	m^2/g	195	195	00	354	403	284	302
CTAB surface area	m^2/g	175	350	50	271	302	232	256
DBP absorption	g/100 g	263	335	21.5	281	287	265	296
Tapped density	g/l	280	180	36.7	200	185	217	222
Alpine sieve residue 63 μm	%	80	> = 20		99	91	99	52
Alpine sieve residue 180 μm	%	> = 4	1		82	18	87	4.5
Alpine sieve residue 250 μm	%	n.d.	n.d.		75	1.1	48	

Performance properties of the silica of the invention

Flow properties of the silica

The products prepared in accordance with the invention, of Examples 1-3, have very good intrinsic flowability.

	Method	Unit	Description of method	Silica of Ex. 1	Silica of Ex. 2	Silica of Ex. 3
Flow property	Glass efflux vessel	(score)		1	1	1
	Conical bed height	[mm]		9	13	8

Maximum choline chloride absorption

The maximum choline chloride absorption provides important information on the absorption capacity of a silica. Since more highly concentrated adsorbates are of advantage, the desire is for as high an absorption capacity as possible. The maximum choline chloride absorption of the inhomogeneous silicas is much higher than in the case of prior art silica products.

Method	Unit	Silica of Ex. 1	Silica of Ex. 2	Silica of Ex. 3	Silica of Ex. 4	Comp. Ex. Sipernat 2200	Comp. Ex. Sipernat 22	Comp. Ex. Hubersil 5170
Maximum choline chloride absorption	[g/100 g]	300	295	268	280	245	240	165

Flowability of a choline chloride adsorbate

In addition to a high absorption capacity for liquids, it is necessary that the resulting adsorbates be readily flowable. As an example, a 50% adsorbate of choline chloride on the corresponding silica was prepared from 66.6 g of a 75% strength aqueous choline chloride solution and 33.3 g of the respective silica, and the flowability was assessed by means of glass efflux vessels and the conical bed height. The inhomogeneous silicas DTT 3120 and

DTT 3140 give advantages over standard silicas here (Hubersil 5170).

	Method	Unit	Silica of Ex. 1	Silica of Ex. 2	Silica of Ex. 3	Comp. Ex. Hubersil 5170
Flow property 50% choline chloride adsorbate	Glass efflux vessel	(score)	2	5	1	6
	Conical bed height	[mm]	18	32	24	> 50

Agglomerate content

The agglomerate content gives important information on whether a silica is suitable for use as a carrier substance. A high agglomerate content is undesirable, since it leads to an adsorbate which is difficult to process. The agglomerate content of a 50% choline chloride consentrate prepared from 100 g of the corresponding silica and 200 g of a 75% strength aqueous choline chloride solution, is very low, at 0.3 - 2.1%, for the inhomogeneous silicas investigated. The comparative silicas have much higher agglomerate contents.

	Method	Unit	Silica of Ex. 1	Silica of Ex. 2	Silica of Ex. 3	Comp. ex. Sipernat 2200	Comp. ex. Sipernat 22	Comp. ex. HiSil SC72
50% adsorbate of choline chloride on Silica	Agglo merate content	[%]	1.3	2.1	0.3	3.7	2.8	2.7

Sorption rate

Another important parameter for the application is the sorption rate, since in the industrial production of adsorbates the objective is for high throughputs and thus short

residence times in the mixer. In the case of the inhomogeneous silicas investigated, the sorption rate for vitamin E acetate is better than that of the comparative products Sipernat 2200 and Hubersil 5170.

Method	Unit	Silica of Ex. 1	Silica of Ex. 2	Silica of Ex. 3	Silica of Ex. 4	Comp. Ex. Sipernat 2200	Comp. Ex. Hubersil 5170
Sorption rate vitamin E acetate	(score)	2.5	2.5	3.0	2.0	4.5	5

The methods of measuring the flow properties, choline chloride absorption, agglomerate content, and sorption rate are in accordance with the procedures described in "Synthetische Pigmente als Fließhilfsmittel und als Trägersubstanz" [Synthetic pigments as flow aids and carriers], Pigments Brochure Series Nos. 31, Degussa AG, 1992, and also Nos. 1 and 30.

The results of the investigation demonstrate that the inhomogeneous carrier silicas of the invention are suitable for preparing highly concentrated adsorbates, are readily flowable, and produce little dust. This is demonstrated from the example of the absorption of vitamin E acetate and 75% strength aqueous choline chloride solution. Both products are used in the adsorbate form in the feed industry. Also conceivable in practice is the preparation of other highly concentrated adsorbates, such as melamine resins (additive in the rubber industry), acids, e.g., formic or phosphoric acid (feed industry), and pigments, e.g., tagetes extracts (feed industry).

The disclosure of German priority application 10112651.4 filed March 16, 2001 is hereby incorporated by reference into the present application.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.